Vapor Pressure Ebulliometer for Milliliter Samples. Sam R. Hoover, Harry John, and Edward F. Mellon, Eastern Regional Research Laboratory, Philadelphia 18, Pa.

IN STUDIES of the separation of amino acids by distillation of the *N*-acetyl amino acid esters, the determination of the boiling point–vapor pressure relationship of a number of samples was required. Measurements on small samples (<2 ml.) at temperatures of 75° to 250° C. and pressures of 2 to 100 mm. were the essential conditions which had to be met. A survey of the literature revealed no technique that fulfilled these requirements. After numerous unsuccessful attempts to employ the micro-

method of Garcia (*1*), the apparatus shown in Figure 1 was developed. It is a simple adaptation of the Cottrell principle. The larger and more elaborate apparatus described by Willingham *et al.* (*6*) undoubtedly can be used to produce results of great accuracy in the characterization of organic compounds available in quantity. Willard and Crabtree have described a Cottrell-type apparatus which more closely approaches the present design than others, but its use at reduced pressures was not reported (*5*). Ebulliometric measurements and vapor-pressure tensimeter stills have been reviewed recently (*4*).

APPARATUS AND METHOD

The boiling pot and column are of 15-mm. borosilicate glass tubing. The reflux bell is about 35 mm. in diameter. The reflux return tube is 4 mm. in diameter. The side arm, of 10-mm. tubing, has a slight downward slope for about 25 mm., then slopes upward for 50 mm., and has a 25-mm. horizontal portion (out of the photograph) on the end. The 10/30 standard-taper borosilicate glass joint takes a commercial 125-mm. immersion thermometer. The only critical dimension is that which places the thermometer bulb just below the lip of the boiling pot. A 10- to 15-mm. length of 0.5-mm. tungsten wire is sealed through the bottom of the pot. The completed apparatus should be thoroughly annealed.

Apparatus is supported by a clamp around the rubber tubing of the vacuum line on the side arm. The lower portion of the side arm serves as a receiver and the upward sloping portion serves as a condenser. A stream of water is run onto a cloth which is placed over the upward sloping portion of the arm and is drained off through a funnel placed underneath. The tungsten wire projects through a sheet of asbestos paper which is supported immediately below the apparatus. This wire is heated by a microburner, and serves as a point source of heat which minimizes bumping. A partial shield of asbestos around the apparatus may be required at temperatures of 200° C. and above, especially if the apparatus is operated in an air-conditioned or drafty room.

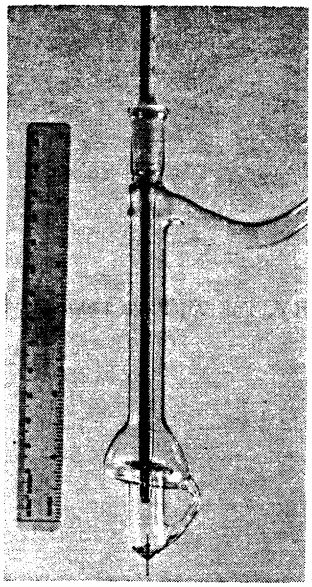

Figure 1. Semimicro-ebulliometer

The sample is added to the pot to a depth of about 10 mm. It should not touch the thermometer bulb even after expansion on heating. Silicone stopcock grease on the thermometer joint is used to lessen the possibility of contaminating the sample. The system is pumped down to the required vacuum, which is maintained by a manostat. The manostat described by Ratchford and Fein (*3*) was used successfully to control the pressure, which was measured by a Zimmerli gage (*7*) to 0.1 mm. A series of determinations at increasing pressures is made. A 10- to 15-minute period in which the reflux is maintained about half-way up the tube between the bell and side arm is sufficient to establish stable pressure and temperature readings. If the purity of the sample is questionable, about 20% of it is distilled into the side arm and the measurements are repeated.

The thermometer is easily calibrated by determining the boiling points of pure compounds which are accepted standards for thermometer calibration. This calibration can be made at atmospheric pressure. The temperatures, reported here, were read to 0.1°.

RESULTS

The ability of this ebulliometer to function as desired was checked by comparing the boiling point curve of a sample of pure capric acid with the data obtained on larger samples by Pool and Ralston (*2*). A log P versus $1/T$ plot of the results is shown in Figure 2. The line was obtained as the least square straight line using all the points obtained by use of the new ebulliometer. Its equation is $\log P = 10.3002 - 3937/T$; 95% of the observed pressures fell within 4% of the pressure values given by the curve. The corresponding equation calculated from the data of Pool and Ralston is $\log P = 10.3719 - 3970/T$; 95% of their observed pressures fell within 9% of the pressure values given by the least square line for their data. Both sets of data are in excellent agreement. The slight difference in slopes and the better precision of the new data are probably due to the larger number of data obtained in this study and to the better control of pressure by modern pressure regulators.

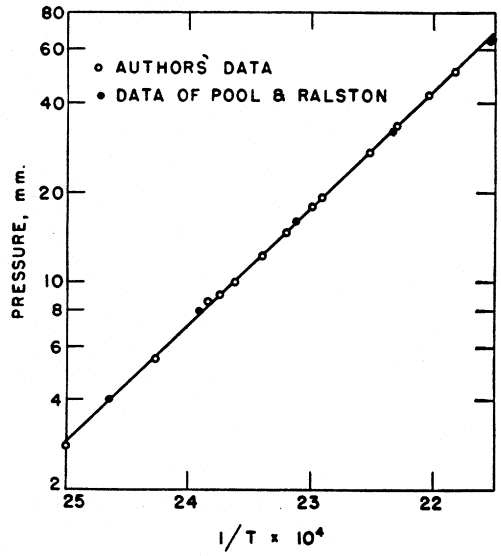

Figure 2. Vapor Pressure of Capric Acid

○ **Authors' data**
● **Data of Pool and Ralston**

This ebulliometer has also been used to determine the vapor pressure–temperature curves of nine acetylated amino acid esters; 70% of the experimental values are within 3% of the values calculated from the equation for the least squares line through the data in the range of 2 to 100 mm. These data will be described in detail at a later date.

This ebulliometer, therefore, is a simple and precise apparatus for the determination of the vapor pressures of milliliter quantities of materials by the boiling point method at all pressures from atmospheric downward.

ACKNOWLEDGMENT

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